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MEMBRANE TECHNOLOGY APPLICATIONS

REPORT NO. 90-139-K

A. Golomb
Water Research Unit
Process Chemistry Section
Chemical Research Department

ABSTRACT

Capability of the newly-established membrane testing and development facility (MTDF) has been demonstrated using bench-scale and pilot scale reverse osmosis (RO) and ultrafiltration (UF) equipment. Good correlation was noted between bench- and pilot-scale operation, particularly for RO. Outlines of opportunities for membrane separation technology applied to (a) the metal-working and surface finishing industries, and (b) the food and beverage industries, are provided. Recommendations for improvements to the MTDF are made.

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EXECUTIVE SUMMARY

MEMBRANE TECHNOLOGY APPLICATIONS

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A. Golomb
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Initial tests have been carried out to demonstrate the capability of the newly-established Membrane Testing and Development Facility (MTDF). Bench- and pilot-scale reverse osmosis (RO) treatment, at 4.1 MPa applied pressure, of a simulated nickel plating waste rinse stream was demonstrated. RO membrane rejection efficiencies for nickel were 99+% (in the bench scale test) and 99.9+% (on the pilot scale). Volume reduction factors of about 25 were attained, at purified water flux rates in the range 1 to 1.5 m^3/m^2 per day. Good correlation was noted between bench-scale and pilot-scale RO test results. Pilot-scale ultrafiltration (UF) of a simulated industrial cutting oil/water waste emulsion at 0.40 MPa gave 99+% oil rejection (pilot scale) at a flux rate of 0.7 m^3/m^2 per day. A volume reduction of about 5.2 was attained. Overviews of opportunities for membrane separation technology applied to (a) the metal cutting and surface finishing industries and (b) the food and beverage industry are given. Capabilities (and some present needs) of the MTDF are outlined, with recommendations.

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research division

TO: Mr. J.E. Mitchell
Manager, Technical Services
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MEMBRANE TECHNOLOGY APPLICATIONS

A. Golomb

1.0 INTRODUCTION

As part of Ontario Hydro's 25-year demand-supply strategy, there is continuing emphasis on increasing the efficiency of utilizing the Province's electrical energy system. To this end, a Membrane Testing and Development Facility (MTDF) has been established at Ontario Hydro Research Division. The MTDF comprises bench-scale and pilot-scale reverse osmosis (RO) and ultrafiltration (UF) systems. RO and UF are membrane separation technologies which with microfiltration (MF) have found numerous industrial applications in wastewater treatment and/or by-product recovery. Since no phase change is involved in RO and UF, they are more energy efficient separation processes than, say, evaporation or distillation. Each is briefly discussed below.

Reverse Osmosis

Reverse osmosis occurs when a dilute aqueous solution is pumped, under an applied pressure greater than the solution osmotic pressure, through a chamber lined with a suitably supported semi-permeable membrane/1/. Purified solvent (water) preferentially passes through the membrane and is collected as permeate for reuse or discharge as appropriate. Solutes are rejected by the membrane. The retentate, relatively concentrated by removal of solvent, may either be recovered for reuse or discharged after treatment as appropriate.

The solution osmotic pressure that has to be overcome is a limiting factor for RO, since high applied pressures may cause ineversible membrane compaction. RO is therefore restricted to fairly dilute solutions. For many years, the most widely available commercial RO membranes have consisted of anisotropic films of cellulose acetate. These membranes comprise a dense solute-rejecting ultrathin layer supported integrally on a porous substructure of the same material. Cellulose acetate membranes have the dual advantages of low cost, and high solute-solvent separation efficiencies. They suffer, however, from disadvantages that include poor chemical resistance to oxidizing agents, strong acids and bases, vulnerability to attack by cellulolytic bacteria, poor temperature resistance (above 45°C), and a tendency to undergo irreversible compaction with loss of performance at elevated operating pressures (above, say, 7.0 MPa).

In recent years fully-synthetic RO membranes have been developed and fabricated commercially as thin film composites (TFC's), consisting of an ultrathin rejecting layer of one polymer

superimposed on a porous supporting layer of another. Such combinations have generally good chemical, bacterial and thermal stability in addition to good compaction resistance. Although they are more expensive than cellulose acetate RO membranes, TFC membranes perform well and are considerably more durable under a much wider range of physical and chemical operating conditions in areas of industrial application for which the earlier membranes are unsuitable/2/.

Ultrafiltration

Ultrafiltration occurs when an aqueous solution containing dissolved macromolecules or colloids is pumped at a low applied pressure (up to, say, 0.7 MPa) through a chamber lined with a suitable-supported membrane which permits passage of solvent (water) and low-molecular weight species/1,2/. Dissolved or colloidal macromolecules that exceed a certain molecular weight (ie, the molecular weight cut-off, or MWCO) are rejected. UF membranes are characterized by high permeation rates for water at low applied pressures. Polymeric solutes, colloids and/or suspended particles can be fractionated on the basis of size using UF. Commercial UF membranes are made of anisotropic porous materials, including cellulose acetate, ceramics (eg α-alumina) and fully-synthetic polymers such as polysulphones. Non-cellulosic UF membranes are especially stable toward a wide range of chemical conditions, and are resistant toward strong acids and bases, oxidizing agents, bacterial attack, and elevated temperatures/2/.

RO/UF Systems

Commercially available RO/UF membrane systems come in four basic modular configurations. These are:

- plate and frame
- tubular
- spiral wound, and
- hollow fibre

As described in some detail in the recent Ontario Hydro publication "Membrane Technology Reference Guide/3/, each type has certain advantages and disadvantages for a given application. In North America today, the most widely used RO/UF membrane modules appear to be of the spiral wound type. In general, tubular modules have the advantage of being the most capable of handling suspended solids without irreversible membrane fouling. However, the membrane packing density (surface area/unit volume) is low, so that a relatively large floor space is required. On the basis of membrane area, tubular membranes are generally more expensive than spiral wound membranes. While spiral wound modules have a much higher packing density, their feed-side flow channels are narrow, and feed may require more extensive pretreatment to prevent fouling. They are usually run with alternating operating and cleaning cycles as required to maintain adequately clean membrane surfaces and good separation efficiency.

Hollow fibre modules have enormous surface area per unit volume, but because of close fibre packing, have a tendency to foul irreversibly under conditions where suspended matter is present. Plate and frame modules are capable of processing viscous feed streams because of high shear effects in thin flow channels. However, if fouled, they can be difficult to clean without manually disassembling the module.

2.0 MEMBRANE TESTING AND DEVELOPMENT FACILITY

During 1989-90, commercially-available bench-scale and pilot-scale RO and UF membrane testing equipment was acquired and assembled at Ontario Hydro Research Division, Chemical Research Department, forming the nucleus of the Membrane Testing and Development Facility (MTDF). The equipment was chosen with versatility and economy in mind. The RO and UF bench-scale equipment are of plate-and-frame design. In this way very small circular sheets (a few centimetres in diameter) of membrane can be used for preliminary test purposes and, after generating operating

data, can be either discarded, or physically or chemically cleaned for further testing. The pilot-scale RO and UF equipment are each of spiral wound configuration, giving a good balance of high membrane surface packing density and tolerance toward low levels of suspended solids.

Details of membranes currently available at the MTDF for bench scale and pilot-scale RO and UF testing are listed in Tables I and II. Canadian suppliers of RO membranes were Zenon Water Systems Inc. of Burlington, Ontario, who provided flat sheet membranes for bench-scale testing and corresponding pilot-scale spiral wound RO modules (about 6.35 cm diameter x 47.4 cm long). Canadian suppliers of flat sheet UF membranes were Amicon Canada Ltd. of Oakville, Ontario, and Zenon. Pilot-scale spiral wound UF membrane modules (about 6.35 cm diameter x 63.5 cm long) were obtained from Zenon.

Bench-Scale Reverse Osmosis Test Rig

The bench-scale RO test rig (Figure 1) was acquired to pre-test candidate process or wastewater streams before pilot-scale testing. The total combined RO membrane surface area of the twin bench-scale cells is about 28.4 cm^2. A specially fabricated precision ground stainless steel circular cutter is used to make bench-scale RO test membranes from sheet material from the supplier.

The bench scale RO unit was manufactured by the Universal Water Corporation, California, USA. A holding tank is used for the feed/retentate. Pressure is applied by a Milton Roy positive displacement pump of variable stroke length. An in-line Greer-Olaer bladder accumulator evens out pressure pulsation in the system. RO takes place in twin test cells. At intervals, the permeate flow rate is measured, and samples of retentate and permeate taken for analysis. A Grove back-pressure regulator controls the system applied pressure to the desired level, as registered on twin pressure gauges. During a test run, the RO retentate is continuously recirculated back to the feed holding tank. As the concentration of the retentate increases, so does the osmotic pressure that has to be overcome, characteristically resulting in flux rate decline, especially toward the end of the run.

Reverse Osmosis Pilot Scale Unit

The pilot scale RO unit is the Zenon Model PSSP300 HPX reverse osmosis system. The basic model was designed to effectively remove dissolved inorganic salts, organics, bacteria and pyrogens from raw water supplies to give high purity water for selected applications. All wetted metal parts are in sanitary grade stainless steel.

A simplified process and instrumentation schematic of the pilot-scale RO system in the MTDF is given in Figure 2. The major components of the system are:

- prefilter, equipped with a 5 μm cartridge
- two process feed pumps in series (primary pump up to 1.0 MPa and booster pump up to 5.5 MPa)
- RO membrane module housing for 1.11 m^2 spiral wound membrane (Figure 3)
- clean-in-place (CIP) system
- solid state circuitry control system.

These components are interconnected with the necessary piping, valving, wiring and controls, on a self-contained, rugged stainless steel frame. The RO unit stands 1.78 m high, 0.91 m wide and 0.56 m deep. Safety features include a low-pressure switch and a high-temperature switch to shut off the pump system.

Table I

Membranes Available for RO Testing at MTDF

	Supplier	Designation	Manufacturer/Reference Number	Nominal NaCl Rejection (%)
Bench Scale Flat Sheets	Zenon	SW	Filmtec	99
	Zenon	BW	Filmtec	98
Pilot Scale Spiral Wound Modules	Zenon	SW	Filmtec/SW30-2514	99
	Zenon	BW	Filmtec/BW30-2514	98
	Zenon	TW	TW Filmtec/TW30-2521	98

Table II

Membranes Available for UF Testing at MTDF

	Supplier	Designation	Manufacturer/Reference Number	Nominal MWCO*
Bench Scale Flat Sheets	Amicon	YC-05	Amicon	500
	Zenon	G-5	Desalination Systems/GE	600
	Amicon	YM-2	Amicon	1,000
	Zenon	G-10	Desalination Systems/GH	2,000
	Zenon	G-20	Desalination Systems/GK	6,000
	Amicon	YM-10	Amicon	10,000
	Zenon	E-100	Desalination Systems/ER	20,000
	Amicon	YM-100	Amicon	100,000
	Amicon	XM-300	Amicon	300,000
Pilot Scale Spiral Wound Modules	Zenon	G-5	Desalination Systems/GE	600
	Zenon	G-10	Desalination Systems/GH	2,000
	Zenon	G-20	Desalination Systems/GK	6,000
	Zenon	E-100	Desalination Systems/ER	20,000
	Zenon	E-500	Desalination Systems/EW	80,000
	Zenon	UF/RO Hybrid	Desalination Systems/DS-5	200-300

* MWCO = Molecular Weight Cut-off

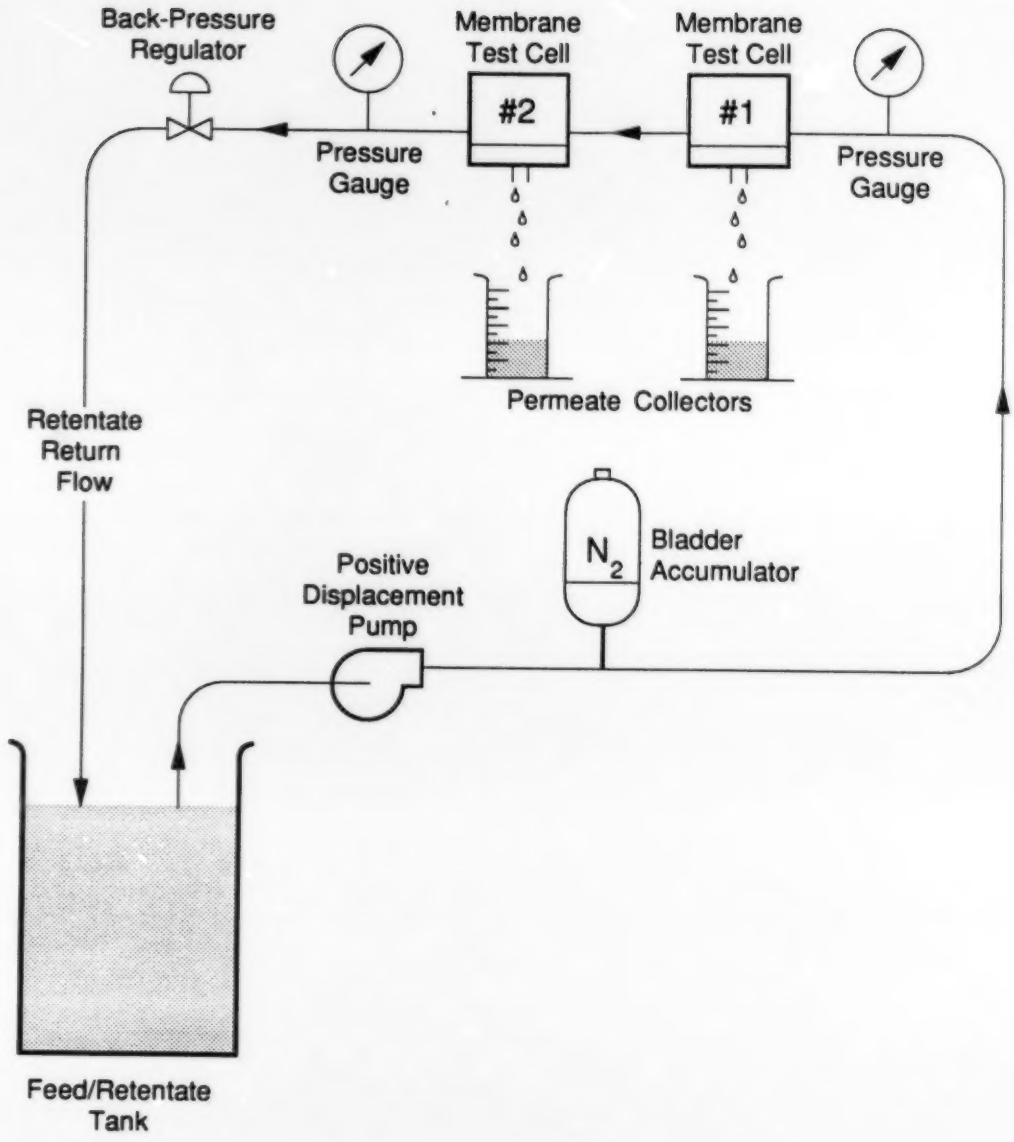
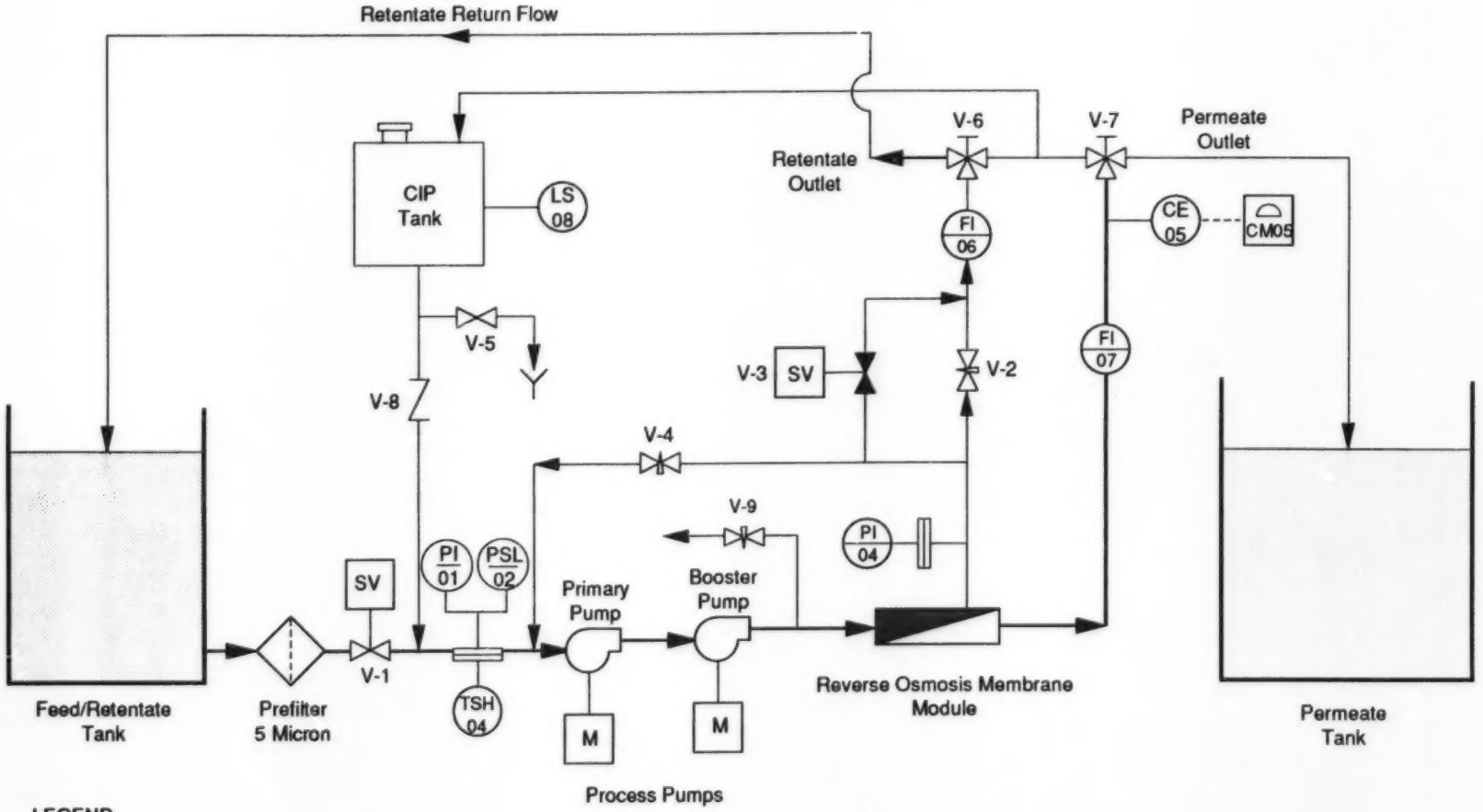


FIGURE 1

FLOW SCHEMATIC OF BENCH-SCALE REVERSE OSMOSIS (RO)



LEGEND

CE	Conductivity Element
CM	Conductivity Meter
FI	Flow Indicator
LS	Level Switch
PI	Pressure Indicator
PSL	Pressure Switch
TSH	Temperature Switch
SP	Sampling Port
SV	Solenoid Valve

FIGURE 2

PILOT-SCALE BATCH REVERSE OSMOSIS SYSTEM

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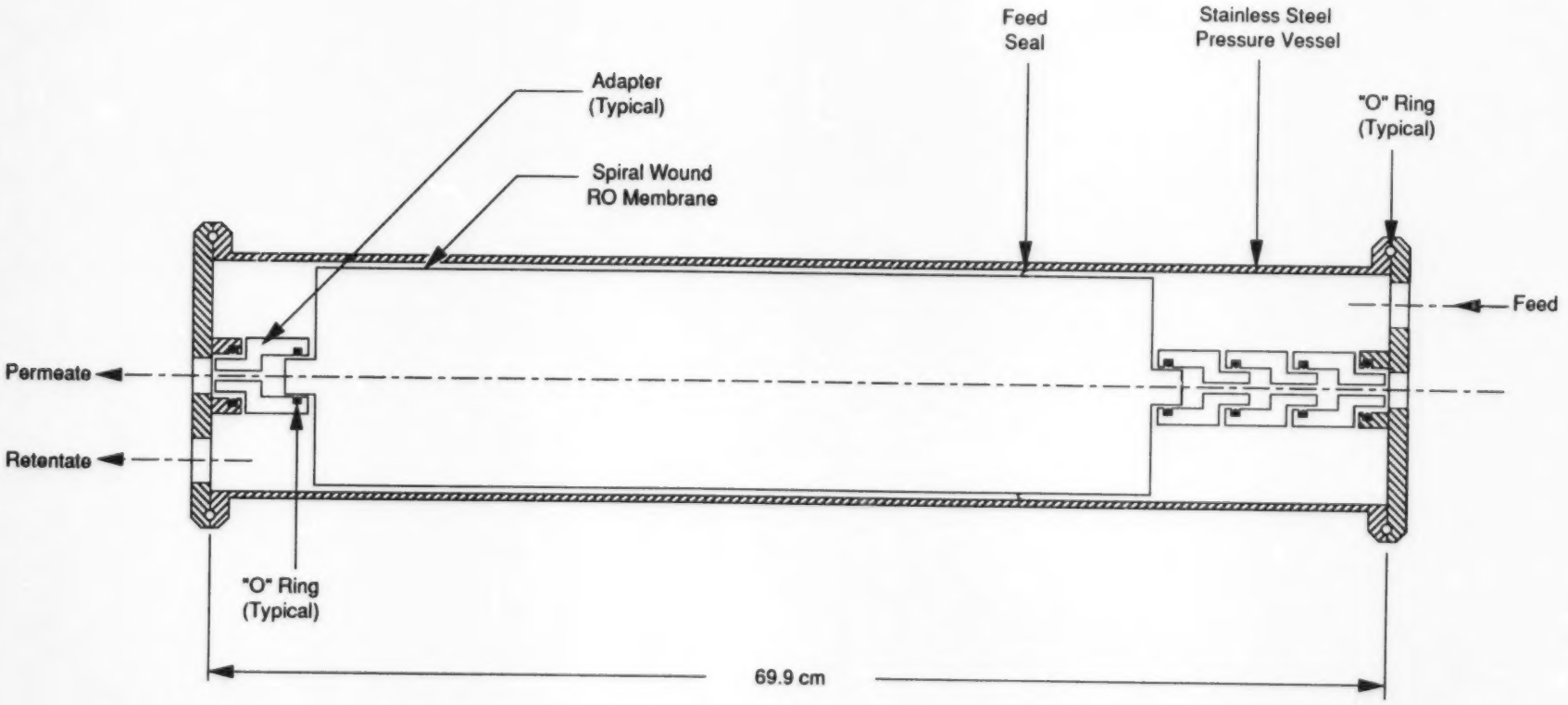


FIGURE 3

**PILOT-SCALE REVERSE OSMOSIS MODULE
(SPIRAL WOUND CONFIGURATION)**

Bench-Scale Ultrafiltration Test Rig

A bench-scale UF test unit was acquired to pre-test candidate process or wastewater streams prior to pilot-scale testing. The advantage of this approach lies in the relatively small membrane area (about 63.6 cm^2) required for preliminary bench-scale UF testing, in contrast with the very much greater membrane area (about 1.86 m^2) required on the pilot-scale UF plant.

An Amicon TCF-10 thin channel UF system (Figure 4) was acquired. This is a self-contained, internally circulating system designed for efficient bench-scale batch concentration and/or fractionation of macromolecular solutions or fine very solid or liquid suspensions.

An integral peristaltic pump recirculates the test fluid through a spiral thin channel flow path, producing high-shear flow with minimal accumulation of solute or suspended matter on the flat membrane surface. This results in effective UF, even at high solute or suspended phase concentrations, where conventional bench-scale UF stirred systems are impractical. A built-in indicator permits operation at optimum pressure and recirculation speed for the feed being processed.

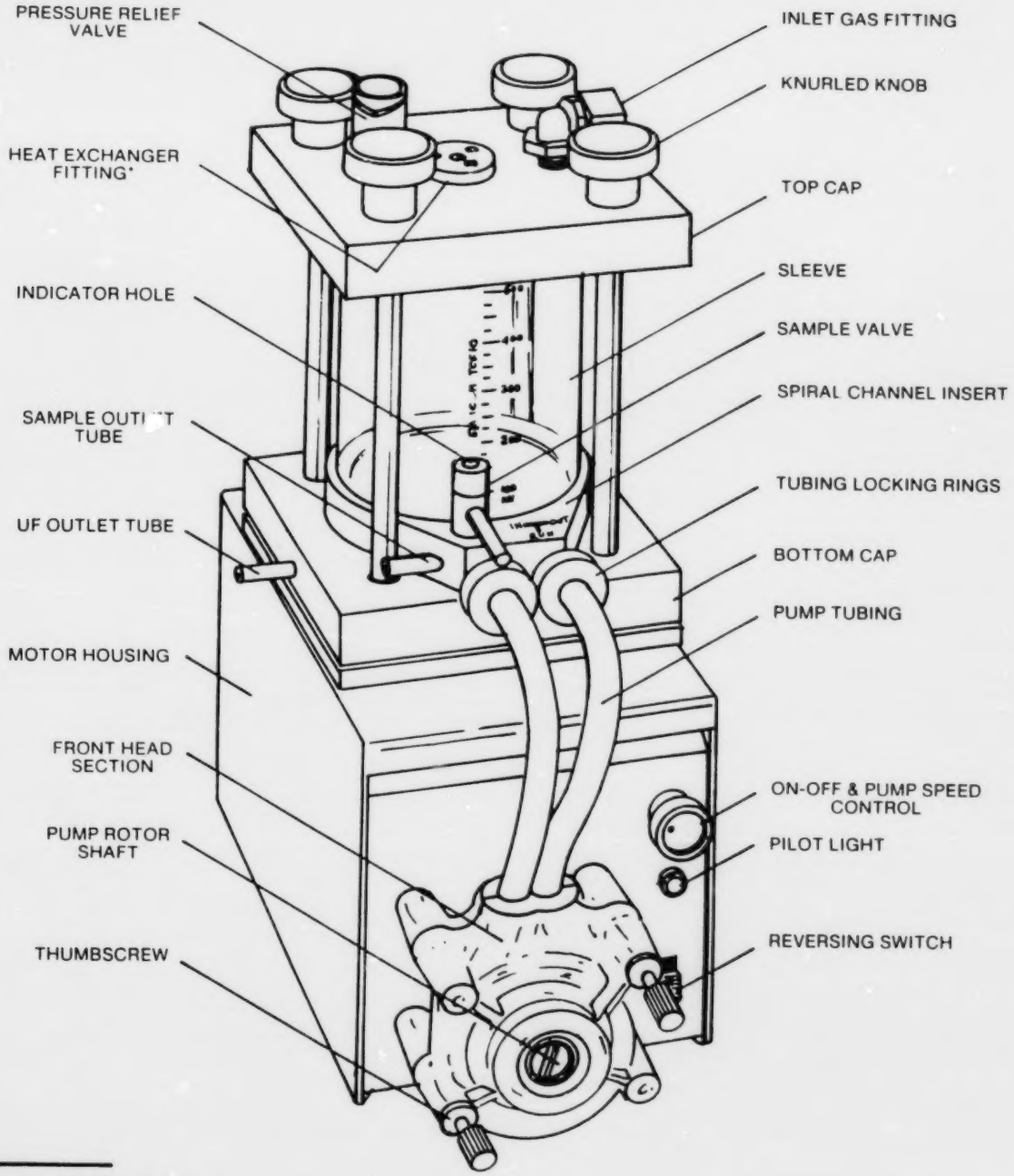
Ultrafiltration Pilot-Scale Unit

The pilot-scale UF unit is the Zenon Model PSSP300UFX, designed to effectively remove high molecular weight organics, bacteria and pyrogens from a raw water source and give high purity water for selected applications. All wetted metal parts are in sanitary grade stainless steel. A simplified process and instrumentation schematic of the pilot-scale UF system in the MTDF is given in Figure 5.

The major system components are:

- prefilter, equipped with a 5 μm cartridge
- process feed pump (delivering up to 0.7 MPa)
- UF membrane module housing for 1.86 m^2 spiral wound membrane (Figure 6)
- clean-in-place (CIP) system
- solid state circuitry control system.

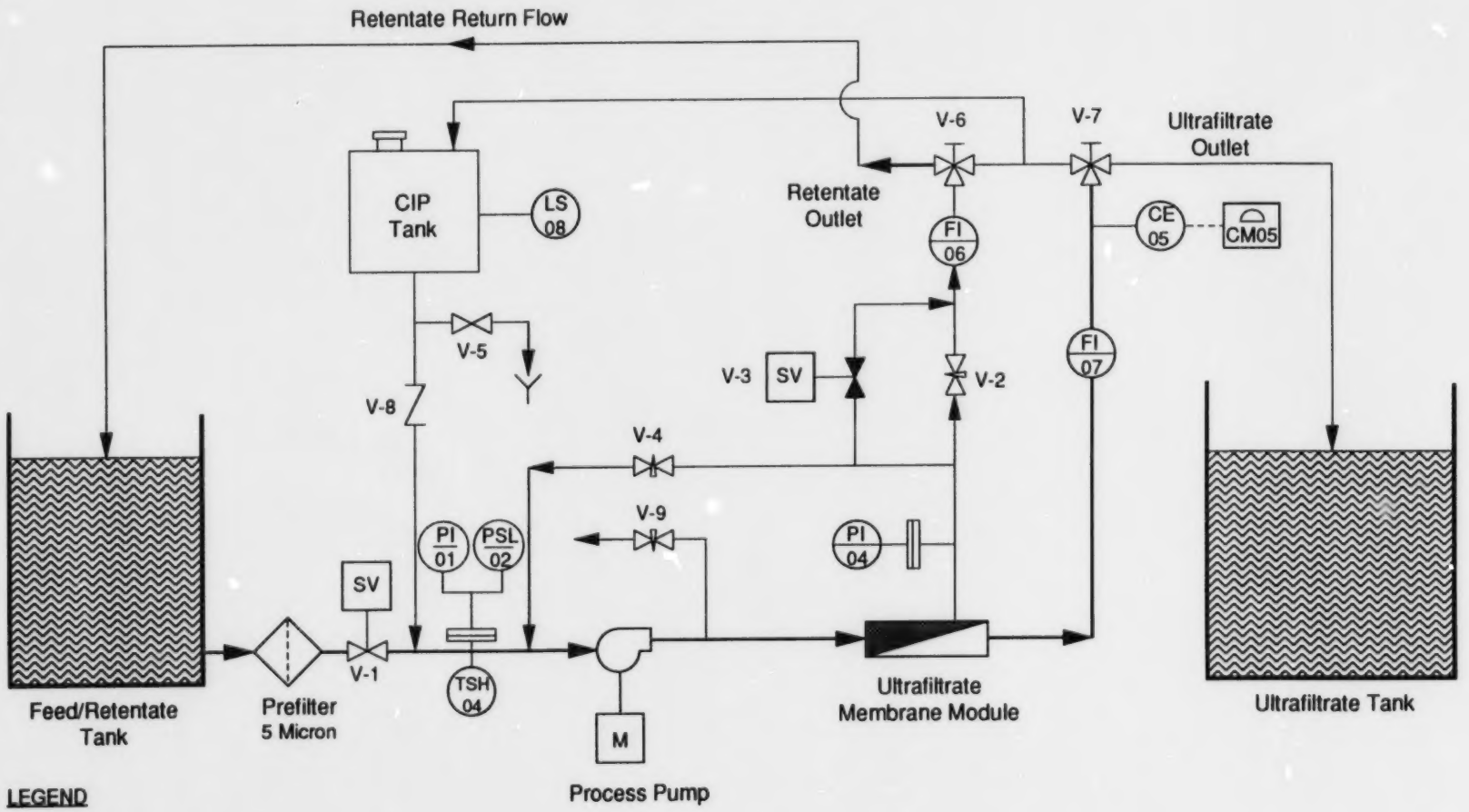
These components are interconnected with the necessary piping, valving, wiring and controls, on a self-contained rugged stainless steel frame. The UF unit stands 1.78 m high, 0.91 m wide and 0.56 m deep. Safety features include a low pressure switch and a high temperature switch to shut off the pump.



*On units with heat exchanger.

FIGURE 4

BENCH-SCALE AMICON TCF-10 ULTRAFILTRATION UNIT



LEGEND

CE	Conductivity Element
CM	Conductivity Meter
FI	Flow Indicator
LS	Level Switch
PI	Pressure Indicator
PSL	Pressure Switch
TSH	Temperature Switch
SP	Sampling Port
SV	Solenoid Valve

FIGURE 5

PILOT-SCALE BATCH ULTRAFILTRATION SYSTEM

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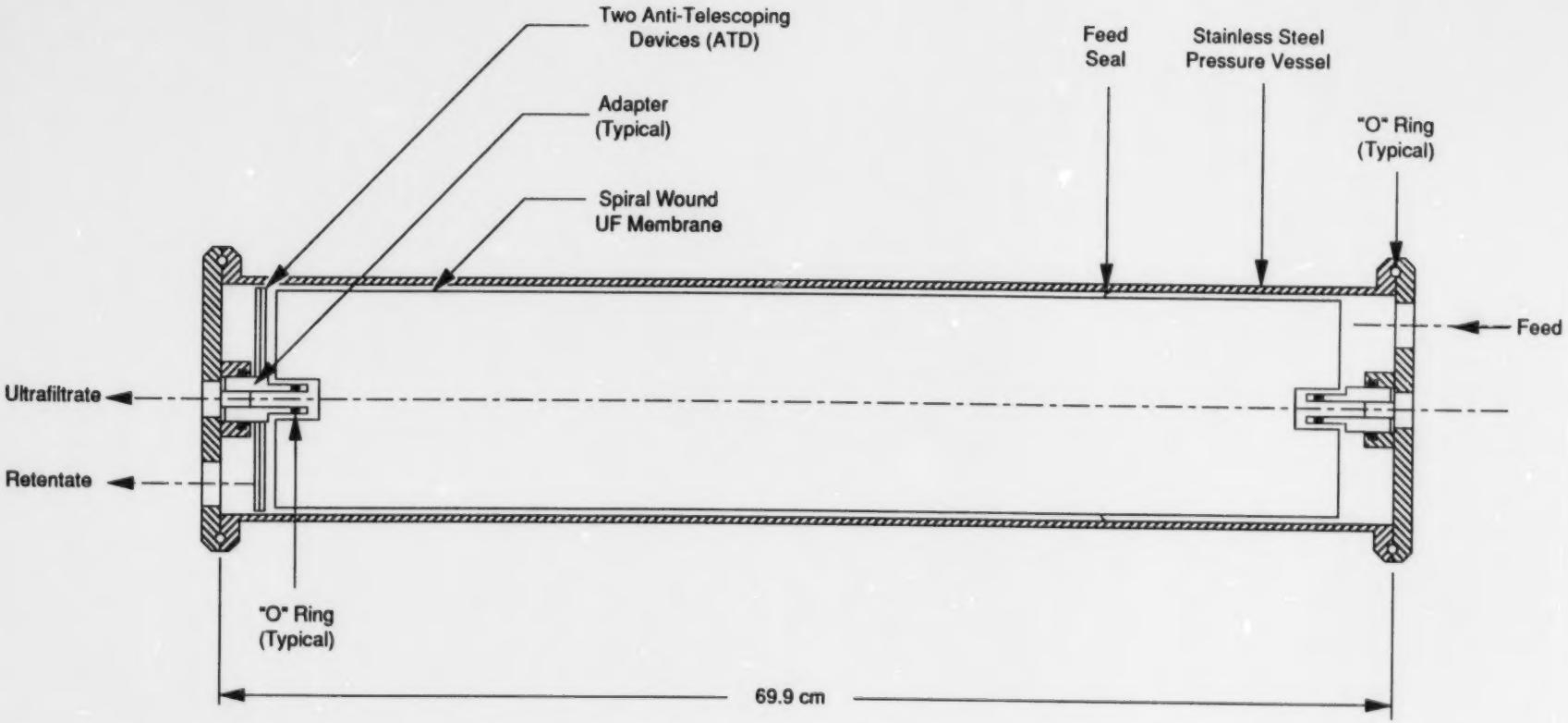

FIGURE 6

PILOT-SCALE ULTRAFILTRATION MODULE (SPIRAL WOUND CONFIGURATION)

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3.0 AREAS OF INDUSTRIAL APPLICATION OF RO AND UF

Food and Beverage Industry

Membrane filtration is often the most effective way to concentrate, fractionate or clarify a liquid stream in the food and beverage and other industries/1,2,4/. In conventional, 'dead-end' filtration, all of the liquid flows through the filtering medium and a superimposed layer of residual filter cake of variable thickness. In crossflow RO/UF membrane filtration, on the other hand, the liquid flows in a sweeping action parallel to the membrane surface, keeping it relatively clean and free from settled material. Formation of a filter cake, as such, is virtually eliminated. This occurs best under conditions of either turbulent flow (RO/UF) or high-shear laminar flow (UF). The applied pressure causes the water and smaller particles, eg, ions and small molecules to selectively pass through the membrane pores, leaving a retentate enriched in the relatively larger suspended and dissolved particles.

Membrane systems have unique separation capabilities, in addition to lower energy costs than are associated with evaporation or distillation. The beverage industry today is beginning to use both microfiltration (MF) and UF for clarification, eg, in beer production. This is in contrast with previous, almost exclusive use of diatomaceous earth 'dead-end' filtration. To effectively replace conventional techniques with membrane systems, the latter must give continuously high permeation rates and be free from significant fouling.

Membrane systems - RO, UF and (increasingly) MF - currently have application in the food and beverage industry as follows. (The list is by no means comprehensive.)

Dairy Products

- Concentration of milk in cheese making to increase yield by incorporating some of the whey protein in the cheese/5/.
- Partial concentration of whey to reduce evaporator or dryer energy loads/6/.
- Fractionation of whey, to separate proteins from lactose and minerals before drying/7/.
- Preconcentration of skim milk before making dietary yoghurt and other cultured products, to increase the protein content without increasing lactose/8/. It should be noted, however, where protein/lactose fractionation is being considered, that the lactose must either be sold at a competitive market price compared with other forms of sugar, or discharged if permitted, with attendant sewerage surcharges. Such discharges may be proscribed by law in future as environmental regulations become more stringent.

Juices (RO/UF)

RO has been used for juice concentration/9,10,11/. Today UF is widely used to remove suspended solids, colloids, proteins and condensed polyphenols from fruit juice streams. Enzymatic depectinization of juice prior to UF can be used to increase productivity due to reduced viscosity. Furthermore, 'fining' or settling prior to UF improves juice quality. Advantages of RO/UF of juices include low-cost achievement of the following:

- clarification of grape juice, citrus juices and especially apple juice to remove haze
- clarification of pear, pineapple and cranberry juices
- concentration of juices to, eg, 70° Brix by RO
- decolorization to produce lighter juices.

Juices (MF)

MF of fruit juices permits colour to pass through with the juice while maintaining sufficient juice clarity. This is particularly important in processing such highly-coloured juices as cranberry, red grape and black currant/12/.

Egg Processing

- production of egg protein concentrates/12/

Gelatin

Gelatin has traditionally been produced using diatamaceous earth filtration, followed by ion exchange to remove salts present, and finally evaporation. UF (spiral wound modules) of gelatin solution has been shown/12/ to concentrate and purify the product by permitting inorganic salts and low MW organics to be removed in the permeate. Typically, UF can concentrate a 2% w/w gelatin feed stream to about 20% w/w gelatin.

Water

- purification of food and beverage plant water
- removal of excessive levels of sodium, calcium and magnesium from water to be used in beverages
- removal of micro-organisms (bacteria, viruses, etc) from water in beverage and juice reconstitution.

Wines

- Wineries tend to be competitive and proprietary, and it is often difficult to gauge their usage of membrane technology. Nevertheless clarification of wines would appear to be a logical application for cross-flow filtration/13,14/. A recent study/14/ of the application of membrane electrotechnology to treatment of winery wastewater gave unpromising results due to poor solute rejection (eg, for ethanol).

Vinegar and Pickle Brines

- Clarification of vinegar and pickle brines by cross-flow filtration, eg, turbidity of vinegar (17% acetic acid) can be reduced by 60% by MF and 97-98% by UF.

Maple Syrup

- About 80% w/w of the water to be removed from maple sap can be removed by RO, prior to evaporation and caramelization.

Beer

- Production of low alcohol beer using RO has been reported in England/15/.
- Pilot trials in the USA and Europe have demonstrated that recovery of beer from "tank bottoms" by MF can reclaim up to 5% of the beer, which is considered to be significant/12/.
- Clarification of beer by cross-flow filtration, without need for 'fining' and conditioning with diatomaceous earth, has also been demonstrated.

Wastewaters

- recovery of valuable by-products from wastewaters
- removal of dissolved solids from wastewaters for reuse.

Despite advances in RO, UF and MF membrane separation technology in the last few years, their use in Ontario's food and beverage industry is still in its infancy. There is high potential for application in the dairy, wine, fruit juice and other sectors. This will most likely be realized as processors become more familiar with the technology.

4.0 MTDF DEMONSTRATIONS

Effective demonstration of RO and UF of food and beverage process or related waste streams for product modification or by-product recovery requires aseptic handling conditions. Commercially, such conditions are scrupulously maintained to avoid contamination and/or bacterial spoilage. At Ontario Hydro Research Division, such an environment is not yet available for the MTDF. It was therefore decided to postpone direct demonstration of food and beverage application, and to focus initial efforts at the MTDF on demonstrating other commercial RO and UF processes, using the bench- and pilot-scale RO/UF equipment. Treatment of nickel plating rinse water by RO, and of cutting oil/water emulsion by UF, were chosen for demonstration. Each of these is described in turn below.

Nickel Plating Waste Rinse Waters

In Canada, and Ontario in particular, the electroplating industry has borne its share of concern over pollution of our water resources. Government regulatory agencies are continuously reviewing and revising permissible limits of heavy metals and other contaminants that can legally be discharged to water courses. Apart from being directly toxic to human beings and wildlife, many of these substances poison the bacteria that carry out the processing of organic matter in wastewater treatment plants. Moreover, plating waste rinse waters contain substantial quantities of potentially recoverable valuable resource materials. The Ontario MOE's MISA program has already addressed the plating sector, with far-reaching consequences.

Given the wide variety of operating conditions found in plating practice, recovery systems must be tailored individually to each operation. Ideally, a plating rinse water treatment system would operate "closed loop", ie, with virtually complete recycle of water and chemicals. This can most simply and inexpensively be achieved using countercurrent rinsing. In a new plant, if a sufficiently high number of countercurrent rinse stages can be installed, rinse solution from the first stage can be returned to the plating bath to make up for evaporative losses. For an existing plating line, however, where it is impractical to introduce a sufficient number of rinse stages, some alternative method must be sought. In North America today, evaporation, ion exchange and RO systems/16/ have been incorporated in plating installations for recovery and recycle of metals and purified rinse water. If organic brighteners are used in the plating bath, these may gradually degrade. Their decomposition products would accumulate and contaminate the bath. An activated carbon filter in the RO concentrate return line would remove such contaminants and is recommended. While RO has found fairly wide acceptance in the US plating industry, especially for nickel rinse recovery, there appears to have been no corresponding degree of acceptance in Ontario. (In contrast, UF has found application in treatment of dragout/rinse waters from electrophoretic painting of truck cabs, both in the US and in Ontario, Canada.)

Waste Cutting Oils

In metal cutting operations, emulsified oil/water coolants (about 3% w/w oil) are commonly used. These eventually turn rancid because of bacterial action, and have to be disposed of from time to time. In a large plant, haulage costs of the waste emulsion to a disposal facility are significant. UF

has been successfully used in the US and Canada to concentrate the waste emulsions to about 15-30% oil w/w/17/. The UF retentate has a much smaller volume than the original emulsion, resulting in correspondingly reduced haulage costs., Alternatively, the retentate may be incinerated on-site and its thermal value recovered. The ultrafiltrate, having an extremely low oil concentration, can be discharged to drain, perhaps without further treatment, and with minimal penalty.

4.1 R.O. DEMONSTRATION WITH NICKEL PLATING RINSE WATER

Application of RO to treatment of Watts nickel plating rinse water was demonstrated on (a) the bench-scale RO unit and (b) on the pilot-scale RO unit. The RO membrane selected for these demonstrations, Zenon BW membrane, had a nominal sodium chloride rejection efficiency of 98%.

4.1.1 Bench-Scale RO

A simulated Watts nickel plating rinse water was made up by diluting with deionized water a standard Watts bath of the following composition:

Total Ni	78 g/L
Total $NiSO_4.7H_2O$	300 g/L
$NiCl_2.6H_2O$	60 g/L
H_3BO_3	30 g/L

A batch sample (19.9 L) of the simulated nickel rinse water was processed at an applied pressure of 4.1 MPa, with recycle of the concentrate, until the retentate volume was 0.57 L, corresponding to a volume reduction factor of about 35. The results are summarized in Table III, and shown graphically in Figure 7.

Membrane rejection efficiencies for nickel were consistently 99+% throughout. The mean flux rate was about 1 m^3/m^2.day, which is a typical, industrially acceptable permeation rate. The permeate was pure enough for recycle as rinse water in a nickel plating operation.

4.1.2 Pilot Scale RO

A larger batch (670 L) of simulated nickel plating rinse water was subsequently processed on the pilot RO unit at 4.1 MPa applied pressure. The concentrate was recirculated in the system while permeate was removed. The results are summarized in Table IV, and shown graphically in Figure 8. Membrane rejection efficiencies for nickel were consistently 99.9+%. The run was halted when the limiting hold-up volume (about 40 L) of retentate in the RO system was reached. This corresponds to a volume reduction factor of about 17. The mean flux rate was about 1.5 m^3/m^2.day, which is industrially acceptable. (It is thought that the reason for the lower mean flux rato (1 m^3/m^2.day) encountered in the bench-scale run is that the flux rate fell due to membrane fouling during the relatively lengthy bench-scale run and had to be restored by careful cleaning of the membrane with a wet cotton swab. A very fine brown gelatinous deposit, presumably iron oxyhydroxide, was removed.)

4.1.3 Energy Consumption

Continuous recirculation of feed/retentate during the pilot-scale batch RO run was accompanied by development of heat. It was necessary to use a simple tap water (4°C) cooled cooling coil in the retentate tank to keep the system well below 40°C, above which the temperature switch would have shut down the primary and booster RO pumps. The energy efficiency of the pumps was not known -- nor was it possible to calculate direct heat losses from the RO system to ambient.

From data given in other sources, however, it is estimated that RO electrical energy consumption is about 6.6 kWh/m^3 of permeate, operating on a scale of about 0.8 m^3/min RO product water.

Table III

Summary of Bench Scale R.O. Using Simulated Watts Nickel Plating Rinse Water
(Zenon BW Membrane: Area = 0.001419 m^2 per cell)

			Retentate			Permeate Cell #1			Permeate Cell #2		
Operating Time (h)	Applied Pressure (MPa)	Conc. Flow Rate (mL/min)	Volume (L)	Temp (°C)	Ni Conc. (mg/L)	Flux Rate ($m^3/m^2/day$)	Ni Conc. (mg/L)	Ni Rejection (%)	Flux Rate ($m^3/m^2/day$)	Ni Conc. (mg/L)	Ni Rejection (%)
0.00	4.1	350	19.90	23.0	705	0.00	0	0	0	0	0
3.00	4.1	350	19.10	22.2	765	1.43	7.4	99.3	1.66	8.0	99.0
27.50	4.1	350	15.00	21.4	955	1.16	5.7	99.4	1.35	5.9	99.4
48.75	4.1	350	11.60	22.4	1205	1.27	8.6	99.3	1.40	10.0	99.1
76.25	4.1	350	8.20	23.0	1790	1.02	11.0	99.4	1.10	11.7	99.4
114.75	4.1	350	3.40	23.5	3820	0.75	18.3	99.5	0.89	19.2	99.5
138.25	4.1	350	1.20	25.6	9320	0.63	42.1	99.6	0.74	53.5	99.4
149.25	4.1	350	0.57	23.0	21240	0.42	111.0	99.5	0.43	160.0	99.3

RO Volume Reduction Factor for Watts Nickel Rinse Water = 35

BENCH SCALE REVERSE OSMOSIS RECLAMATION OF WATTS NICKEL PLATING RINSE WATER

OPERATING PRESSURE=4.1 MPa AT 23° C

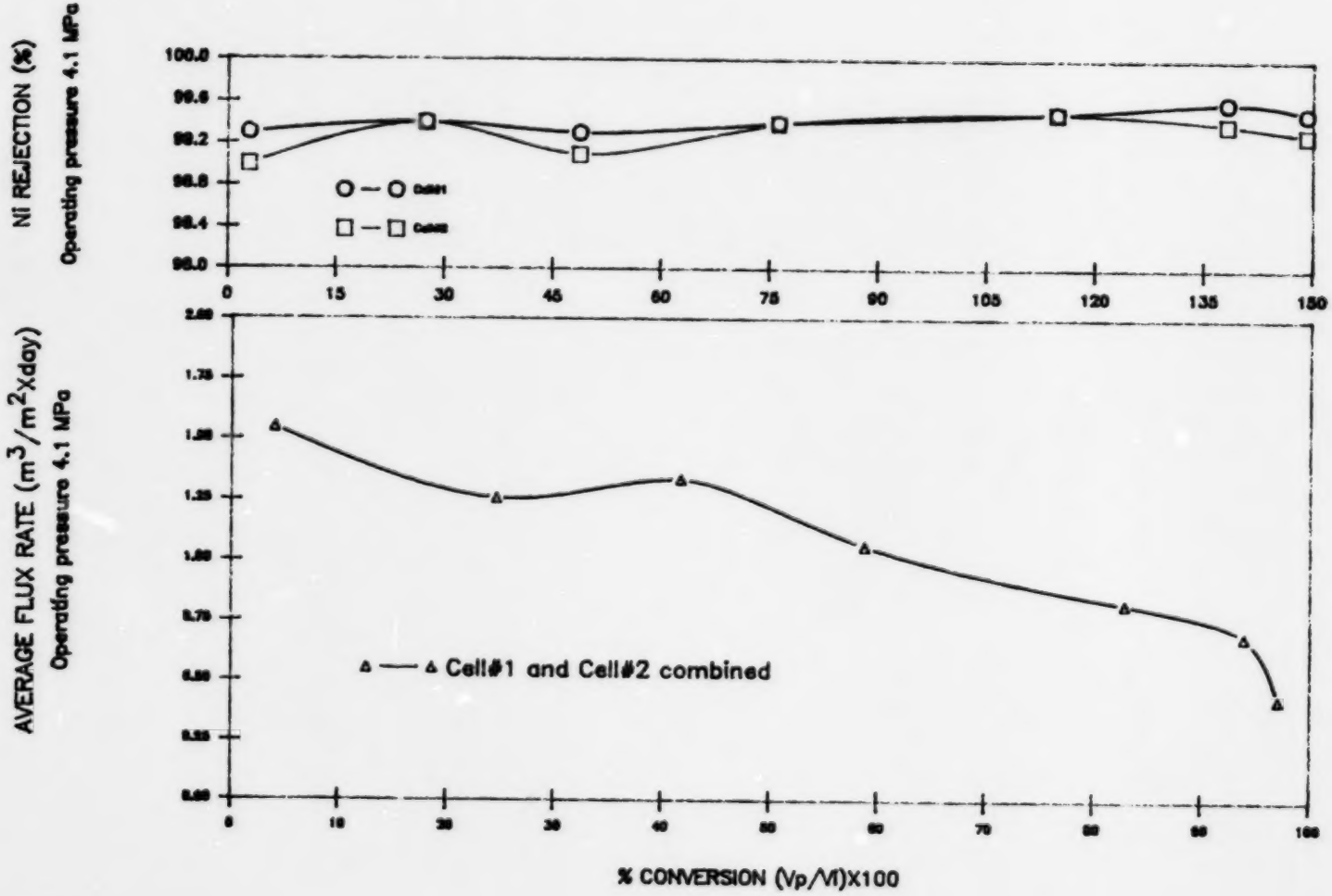

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Figure 7

Table IV

Summary of Pilot Scale R.O. Using Simulated Watts Nickel Plating Rinse Water
(Filmtec Spiral Wound BW 30-2521 Membrane: Area = 1.11 m²

			Retentate			Permeate				
Sample No.	Operating Time (min)	Operating Pressure (MPa)	Volume (L)	Ni Conc. (mg/L)	Total Ni in Tank (g)	Flowrate (L/min)	Ni Conc. (mg/L)	Total Ni in Tank (g)	Flux Rate ($m^3/m^2/day$)	Nickel Rejection (%)
0	0	4.1	670	765	512.6	1.56	0	0	1.98	99.91
1	33.7	4.1	620	855	530	1.37	0.71	0.036	1.74	99.92
2	113	4.1	510	1000	510	1.24	0.76	0.12	1.58	99.92
3	205	4.1	390	1315	512.8	1.22	0.85	0.22	1.55	99.94
4	299	4.1	300	1630	489	1.29	1	0.31	1.64	99.94
5	366	4.1	210	2290	481	1.04	1.24	0.42	1.32	99.95
6	477	4.1	105	4030	423.2	0.93	2	0.63	1.18	99.95
7	582	4.1	40	11640	465.6	0.58	4.43	0.97	0.74	99.96

RO Volume Reduction Factor for Watts Nickel Rinse Water = 16.75

PILOT SCALE REVERSE OSMOSIS RECLAMATION OF WATTS NICKEL PLATING RINSE WATER

OPERATING PRESSURE=4.1 MPa NORMALIZED TO 23 °C

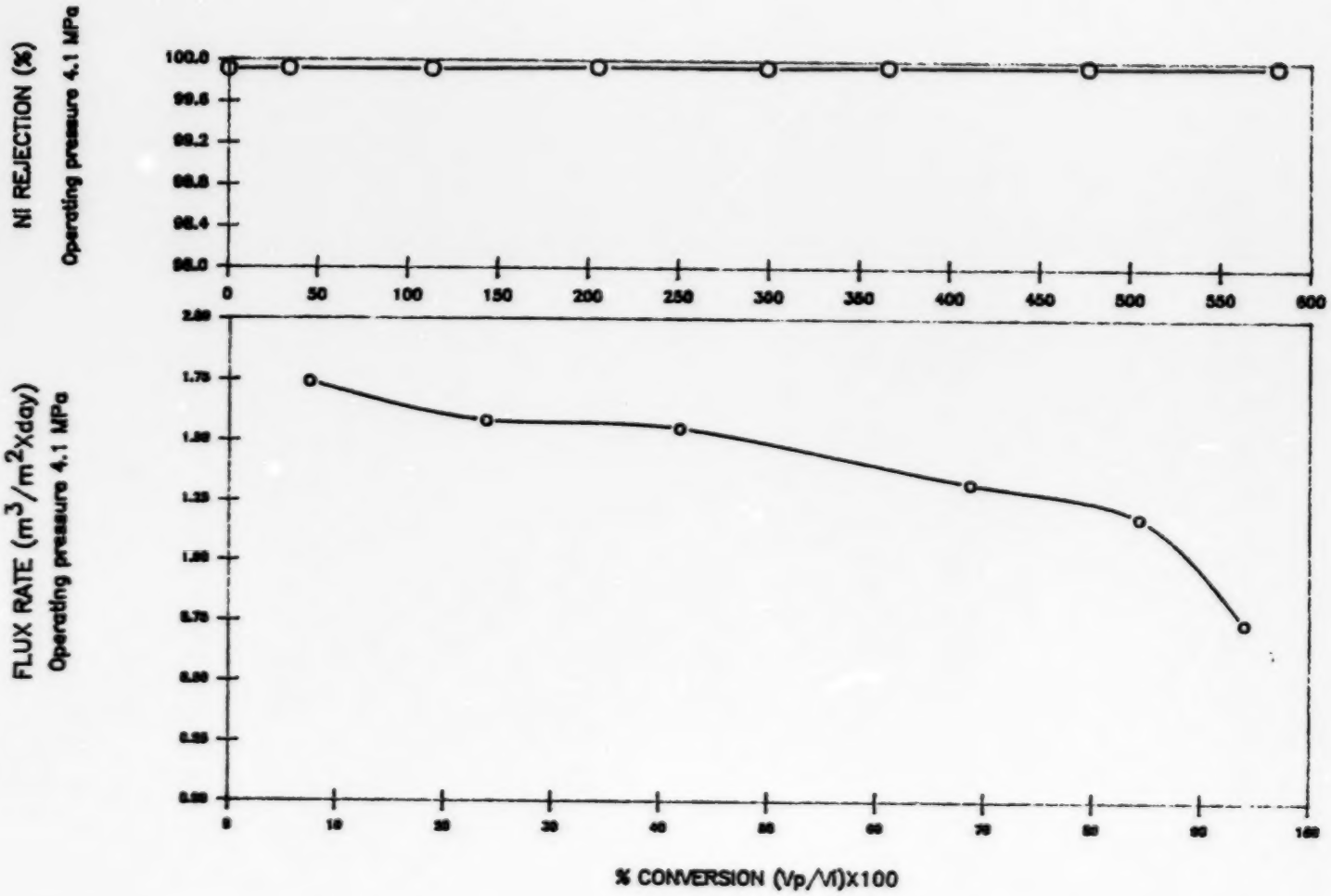

Figure 8

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Evaporation using vapour recompression on the same scale of operation, requires about 23 kWh/m^3 of water removed, ie, evaporation is about 3.5 times more energy intensive than RO.

4.2 UF DEMONSTRATION WITH OIL/WATER EMULSION

The principle of applying UF to treatment of waste cutting oil/water emulsions was demonstrated (a) on the bench-scale UF unit, and (b) on the pilot-scale UF unit.

4.2.1 Bench-Scale UF

A simulated waste cutting oil emulsion was made up, containing about 3% w/w of Shell Dromus B cutting oil and about 97% w/w of water. The UF membranes selected for initial trial, Amicon YM-10 (MWCO = 10,000) and Zenon E-100 (MWCO = 20,000) both gave initially poor ultrafiltration rates that rapidly deteriorated further due to coalescence of the emulsified oil at the membrane surface, with irreversible fouling. When Zenon G-10 (MWCO = 2,000) membrane was used, it gave better performance in that it did not clog rapidly with oil. As shown in Table V, a volume reduction factor of 4.4 was attained, at 0.27 MPa applied pressure. The modest flux rate declined from about 0.2 m^3/m^2.day to about 0.03 m^3/m^2.day over the 7-h run.

Finally, Zenon G-20 (MWCO = 6,000) membrane was tried. It is a relatively "loose" membrane and could reasonably be expected to give faster ultrafiltration rates than G-10. A batch sample (350 mL or 339 g) of the cutting oil emulsion was processed with Zenon G-20 at an applied pressure of 0.27 MPa. Results with G-20 are given in Table VI, and shown graphically in Figure 9 with those of G-10 for comparison. The final retentate volume for G-20 was 52 mL, corresponding to a volume reduction factor of about 6.7. The cumulative ultrafiltrate that was collected was practically clear in contrast with the white emulsion/retentate, indicating good oil/water separation performance. However, the quantity of ultrafiltrate was inadequate ($<< 1$ L) for satisfactory quantitative oil analysis to be carried out. The membrane flux rate for G-20 was moderate, about 0.2 m^3/m^2.day, falling to 0.03 m^3/m^2.day over the 7-h run, and was similar to that observed with the G-10 membrane. Further membrane selection was limited by the range currently available at the MTDF.

4.2.2 Pilot Scale UF

114 L of oil/water emulsion, containing about 3% w/w of Shell Dromus oil B, was processed by UF on the pilot-scale UF unit, using a Zenon G20 spiral-wound membrane module. It was found that due to system limitations, the applied pressure could not be reduced below 0.40 MPa. The run was therefore conducted at this applied pressure. Retentate and permeate samples were analyzed from time to time for oil concentration. Results are summarized in Table VII and are presented graphically in Figure 10.

The initial transmembrane flux rate averaged about 0.64 m^3/m^2.day, ie, considerably higher than had been observed during the bench-scale UF test. This is attributed to the higher applied pressure during the pilot-scale UF run. (The bench-scale UF unit could not be operated at as high as 0.4 MPa for comparison, since it is equipped with a fixed nitrogen pressure relief valve set at 0.35 MPa.) The pilot-scale volume reduction factor was 5.3. The oil content of the retentate was found to be about 12% w/w, which in general is high enough for incineration.

Table V

UF Bench Scale Run at 0.27 MPa Using 3% W/W Oil/Water Emulsion (Zenon G-10 Membrane: Area = 0.00636 m^2)

Time (h)	Retentate Volume (mL)	Permeate Flux Rate (m^3/m^2 x day)	Volume Reduction Factor
0.00	350	0.000	-
0.50	321.6	0.198	1.09
1.00	293	0.207	1.19
1.50	261.3	0.225	1.34
2.50	203.3	0.228	1.72
3.50	160.8	0.147	2.18
4.00	139.2	0.132	2.51
4.50	127.1	0.103	2.75
5.25	111.3	0.081	3.14
5.75	103.5	0.062	3.38
6.25	98.4	0.053	3.56
6.75	94.98	0.033	3.68

Table VI

UF Bench Scale Run at 0.27 MPa Using 3% W/W Oil/Water Emulsion (Zenon G-20 Membrane: Area = 0.00636 m^2)

Time (h)	Retentate Volume (mL)	Permeate Flue Rate (m^3/m^2 x day)	Volume Reduction Factor
0.00	350	0.000	-
1.50	266.5	0.196	1.31
2.25	226.7	0.189	1.54
3.25	174	0.189	2.01
4.00	138	0.172	2.54
4.50	116	0.147	3.02
5.00	98	0.121	3.57
5.75	80.2	0.077	4.36
6.50	71.1	0.035	4.92
7.25	66.9	0.026	5.23

UF BENCH SCALE RUN AT 0.27 MPa USING OIL/WATER EMULSION
Zenon type G–20 and G–10 membrane; effective area=0.006361 m^2
Volume of water/oil=30:1; total vol.=350 ml

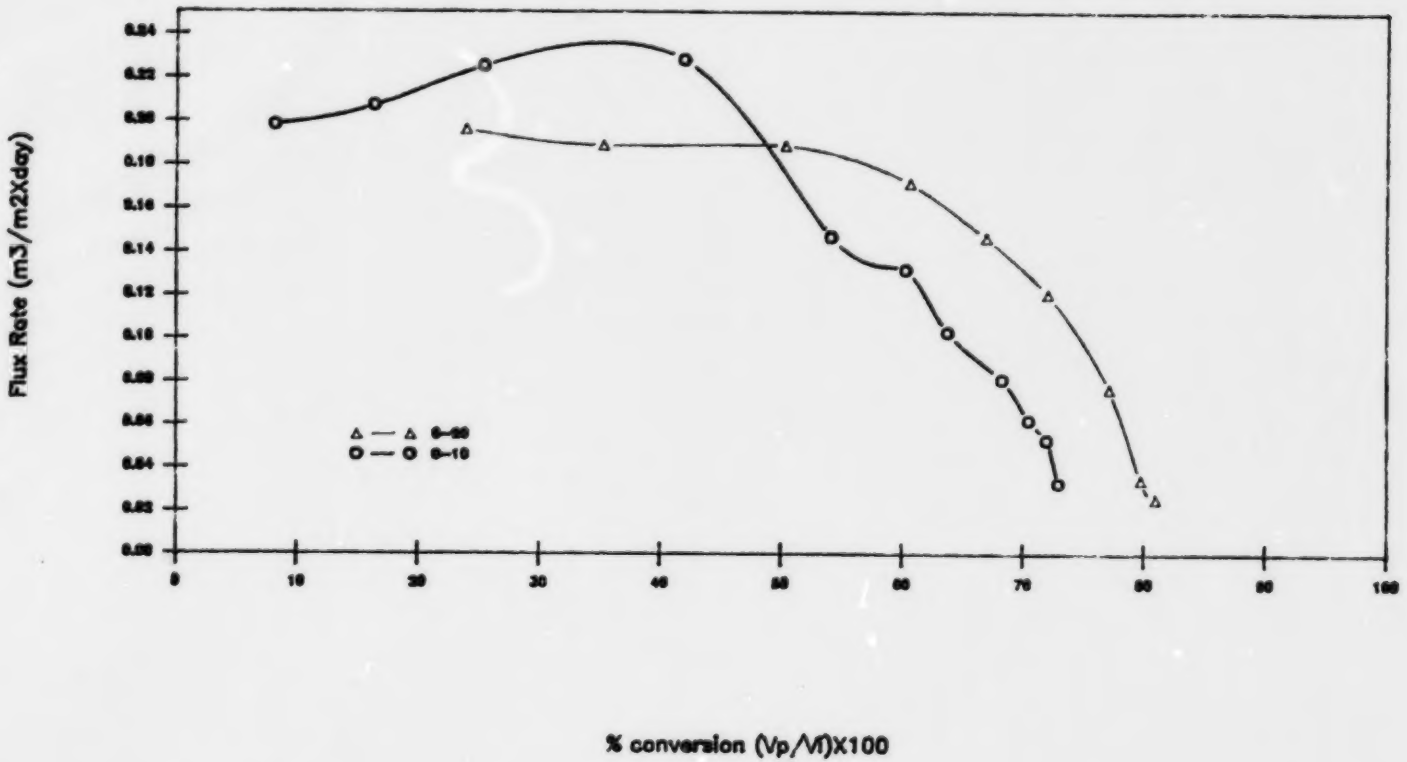

FIGURE 9

Table VII

UF Pilot Scale Run at 0.40 MPa Using 3% W/W Oil/Water Emulsion (Zenon G-20 membrane: Area = 1.86 m^2)

Time (h)	Retentate Volume (L)	Permeate Flux Rate (m^3/m^2 x day)	Volume Reduction Factor	Oil Rejection (%)
0.00	114	0.000	-	-
0.25	100.90	0.663	1.13	-
0.50	87.38	0.663	1.30	99.89
0.70	74.53	0.662	1.53	-
1.00	62.18	0.660	1.83	99.93
1.25	49.20	0.653	2.32	-
1.50	37.80	0.618	3.02	99.93
1.75	26.70	0.574	4.27	99.10
1.80	21.70	0.077	5.25	-

UF PILOT SCALE RUN AT 0.40 MPa USING OIL/WATER EMULSION

Type GK-2525T membrane; effective area=1.858 m2

Volume of water/oil=30:1; total vol.=113.7 L

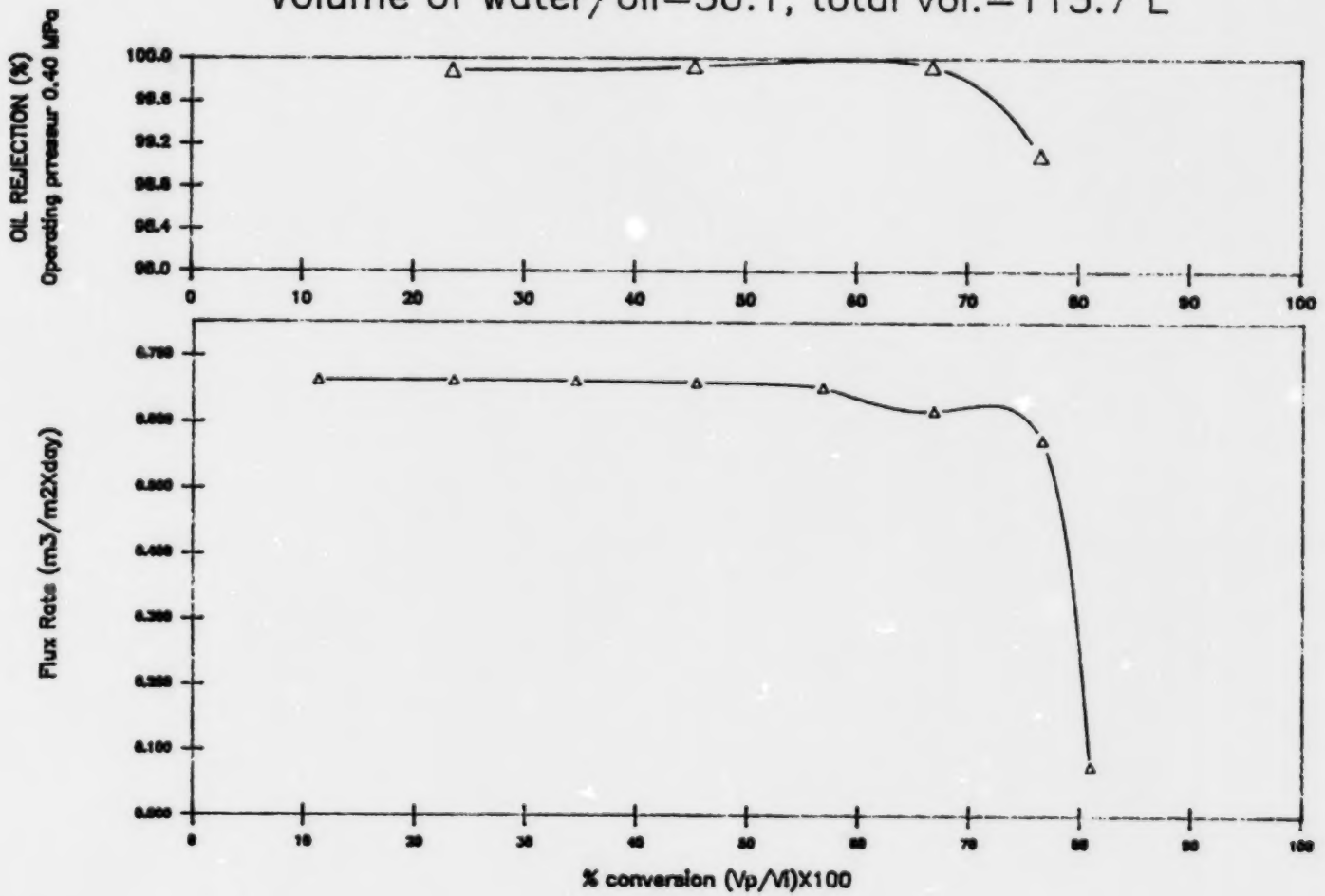

Figure 10

5.0 SUMMARY AND CONCLUSIONS

Demonstrations of low energy-cost membrane technology (reverse osmosis and ultrafiltration) have been carried out at the MTDF.

Bench- and pilot-scale RO treatment of a simulated nickel plating waste rinse stream was carried out at an applied pressure of 4.1 MPa. RO membrane rejection efficiencies for nickel were 99+% (in the bench scale test) and 99.9+% (on the pilot scale). Volume reduction factors of about 25 were attained, at purified water flux rates in the range 1.0 to 1.5 m^3/m^2 day. The purified water was suitable for recycle as fresh plating rinse water. Good correlation between bench- and pilot-scale results was observed.

Pilot-scale UF of a simulated, industrial strength (3% by weight) cutting oil/water waste emulsion was carried out at 0.40 MPa applied pressure. UF membrane rejection efficiency for oil was of the order of 99.9+%, at a flux rate of 0.7 m^3/m^2day. A volume reduction factor of about 5.3 was attained. The clear, purified water contained oil at 30-100 mg/L, which somewhat exceeds the Ontario MOE discharge criterion of 15 mg/L. Process optimization was not carried out, however, since the UF test was for demonstration purposes only. Bench-scale UF tests of the cutting oil emulsion carried out at a lower applied pressure (0.27 MPa, the highest attainable for the bench-scale unit) gave volume reduction factors of up to 5.2. The ultrafiltrate was clear. There was insufficient sample of ultrafiltrate, however, to quantify bench-scale UF membrane rejection efficiency for oil.

Overviews of opportunities for membrane separation technology applied to (a) the metal processing/surface finishing industry and (b) the food and beverage industry are given.

In metal processing, waste cutting oil/water emulsions can be reduced in volume by UF for cheaper haulage to a disposal site. There is also the possibility of discharging the ultrafiltrate, after further treatment as necessary.

In electroplating, nickel waste rinse waters can be reduced in volume by RO and the concentrate (after treatment for removal of organic brightener residues, if required) returned to the plating bath to make up for evaporative losses. The permeate can be recycled as fresh rinse water. "Closed loop" operation of a nickel plating line is possible.

In the food and beverage industry, there are opportunities for application of membrane technology, eg, for clarification or concentration in the wine sector and also in fruit juice production. In the dairy industry there are opportunities for fractionation and/or concentration in manufacture of specialty dairy foods.

6.0 RECOMMENDATIONS

1. It is recommended that opportunities for cost-efficient, low-temperature membrane separation of candidate industrial process and wastewater streams be explored by preliminary screening at the MTDF on a confidential, cost-free basis as a service to Ontario Hydro's industrial customers.

2. To upgrade the present capabilities of the MTDF, acquisition of the following ancillary equipment is recommended:

   (a) Plate-and-frame heat exchanger of stainless steel construction, using 4°C tap water as coolant, to remove about 300,000 cal/min from recirculating pilot-scale RO retentate.

   (b) Disposable prefilter cartridges (0.5 μm) for the RO and UF pilot scale units.

(c) Corrosion-resistant feed pump delivering 0.1 MPa applied pressure to serve RO and UF pilot units.

(d) Replacement bladder to control flow pulsations in the bench-scale RO unit.

(e) Gas regulator with high pressure gas outlet to 6.9 MPa, for recharging bladder accumulator.

(f) Tune-up for Milton-Roy positive displacement pump on bench-scale RO unit.

(g) Flow meters with digital readout for high-turbidity streams.

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REFERENCES

1. S. Sourirajan (ed.), "Reverse Osmosis and Synthetic Membranes. Theory-Technology-Engineering", published by the National Research Council of Canada, NRCC No. 15627, 1977.

2. T. Matsuura and S. Sourirajan (eds.), "Advances in Reverse Osmosis and Ultrafiltration", NRCC No. 29895, Proc. Symposium on Advances in Reverse Osmosis and Ultrafiltration held at Toronto, Ontario, June 7-10, 1989.

3. "Membrane Technology Reference Guide", published by Ontario Hydro, Program Support and Services Division, 1990.

4. A. Woollen, "New Uses for Reverse Osmosis", Food Engineering International, November 1981, pp 42-45.

5. N.C. Beaton, "Ultrafiltration and Reverse Osmosis in the Dairy Industry - An Introduction to Sanitary Conditions", J. Food Protection, 1979, 42, (7), 584.

6. "Energy Management and Membrane Technology in Food and Dairy Processing", Proc. Symposium held at Food and Dairy Expo '83, published by American Society of Agricultural Engineers, 1983.

7. R.C. Lawrence, "The Use of Ultrafiltration in Cheesemaking", paper presented at International Dairy Federation Meeting held in Helsinki, Finland, September, 1987.

8. R.I. Fenton-May, C.G. Hill, Jr., C.H. Amundson, M.H. Lopez and P.D. Auclair, "Concentration and Fractionation of Skim Milk by Reverse Osmosis and Ultrafiltration", J. Dairy Sci., 1972, pp 55, 1561.

9. Anon, "Reverse Osmosis: Ready for Juice?", Food Engineering, February, 1983, p 106.

10. "Anthocyanin Recovery from Cranberry Pulp Wastes by Membrane Technology", J. Food Science, 1980, 45, (4), p 875.

11. B.R. Breslau, B.A. Milnes, J.L. Short and J. Tump, "Ultrafiltration Cuts Fruit Juice Processing Costs", Process Biochemistry, August, 1984, supplement p (iv).

12. J.L. Short, "Newer Applications for Crossflow Membrane Filtration", Desalination, 1988, 70, pp 341-352.

13. "The Application of Membrane Electrotechnology to the Treatment of Winery Wastewater". Report by Zenon Environmental Inc., to Ontario Hydro, December 23, 1987.

14. R.J. Swientek, "Ultrafiltration's Expanding Role in Food and Beverage Processing".

15. A. Mortimer, Technical Director, Elga Ltd., High Wycome, England, personal communication, October, 1989.

16. A. Golomb, "Application of Reverse Osmosis to Electroplating Waste Treatment", Reverse Osmosis and Synthetic Membranes, Chapter 23. NRCC No. 15627, published 1977.

17. T. Krug, Engineer, Zenon Environmental Systems, Inc., Burlington, Ontario, personal communication, June, 1990.